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Preliminary Chemical Aging and Lifetime Assessment for High Density S5370

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Preliminary Chemical Aging and Lifetime Assessment for High Density S5370

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Abstract: A preliminary lifetime assessment of S5370 stress cushions has been performed. Data from three sources were obtained and reviewed to perform this assessment. The sources were the following: 1) the Los Alamos National Laboratory and Honeywell FM&T Kansas City Plant's 2-year and 9-year accelerated aging studies; 2) a large selection of weapon surveillance return data; 3) laboratory experiments at Lawrence Livermore National Laboratory and Honeywell FM&T Kansas City Plant on artificially aged material. The general conclusions of this study are as follows:

1) There is an inherently large degree of structural and chemical heterogeneity in S5370 cushions that complicates lifetime assessments;

2) Current surveillance testing procedures are inadequate for providing insight into aging trends;

3) LANL PMAP data suggests a 60 year load retention of greater than 40%; however, this is for low density versions and extrapolation to high density must be performed with caution and a new set of testing is recommended;

4) Results of chemical aging assessments suggest that radiation damage is minimal at stockpile relevant doses, thermal degradation leads to compression set due to disentaglement of the network structure over time and a negligible amount of chain scissioning at relevant temperatures. The compression set is accelerated by exposure to radiation;

5) In the absence of further testing, a 60-year load retention of greater than 40% is estimated.

1. INTRODUCTION

S5370 stress cushions are crosslinked polysiloxane copolymers filled with an inorganic filler with a porous structure obtained from H_2 outgassing during the curing

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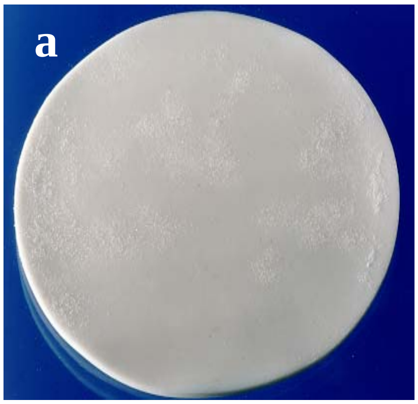

Figure 1. (A) Photograph of S5370 pad. Note density distributions observable from mixture of light and dark sections; (B) Chemical Scheme for synthesis of S5370; (C) Micrograph of diatomaceous earth filler; (D) Tin catalyst used in formulation.

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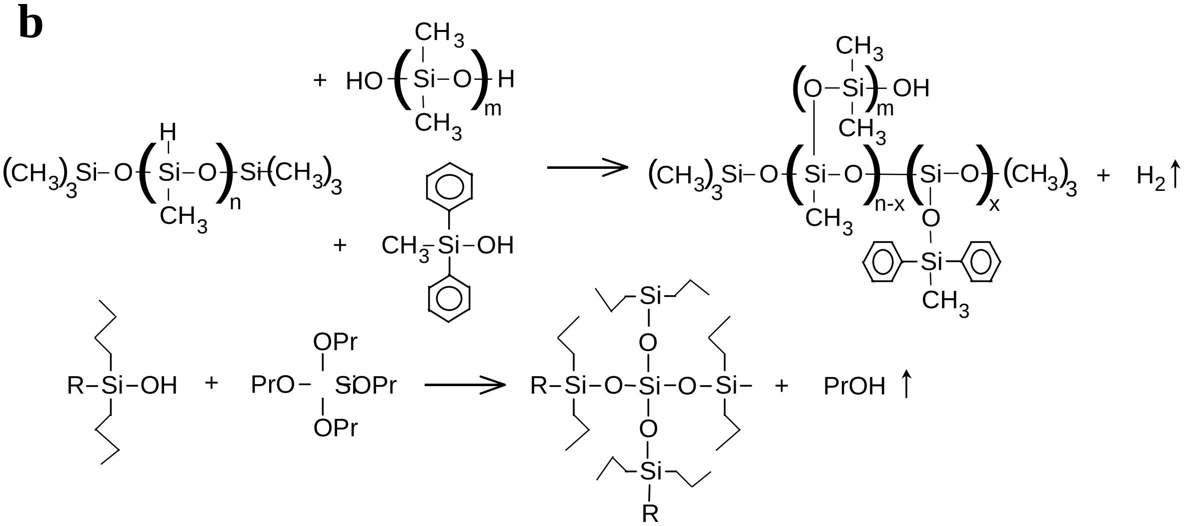

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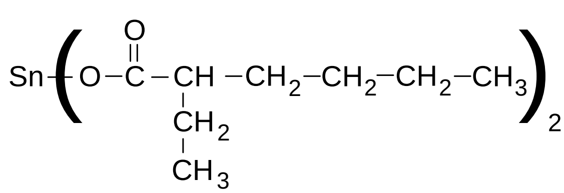


reactions. Two versions have been in use in the stockpile: a low density foam of ~ 60% porosity (0.4 g/cc density) and a high density version of ~ 25% porosity (0.87 g/cc density). The formulation chemistry and some design considerations have been reviewed in a corporate history report published in 1999 by Keith Baker and reviewed briefly in Figure 1.[1] Siloxane chemistry is also reviewed in detail in the text by Brook and Clarson and Senlyen.[2, 3] Details on service conditions can be found in the relevant Certification Plan.[4]

Since these materials serve important functions in weapon systems, quantifying changes occurring in the material's chemical, physical, and mechanical properties over the system lifetime is desirable. In general, however, the stress cushions are subject to numerous potential life limiting degradation mechanisms that are poorly understood, a large variations in service conditions, particularly compression loading, and a large degree of the structural and chemical heterogeneity. The result is a large scatter for the results of standard testing methods and a distinct difficulty in obtaining rational lifetime assessments for these materials.

This report reviews our preliminary efforts to scope out lifetime assessments and aging trends in the high density formulation of S5370. Toward this end, we have initiated a multimode approach including the following: a) a review of data reported by core surveillance; b) a review of the Los Alamos National Laboratory (LANL) Polymeric Materials Assessment Program (PMAP) data on S5370; and c) results of laboratory tests performed on artificially aged S5370 performed at Lawrence Livermore National Laboratory (LLNL), LANL, and the Honeywell Federal Manufacturing and Technologies Kansas City Plant (KCP). To date, the results of these tests are the best basis for lifetime predictions for S5370, although results from studies sponsored by the Enhanced Surveillance Campaign (ESC) may provide additional insight in the coming years.

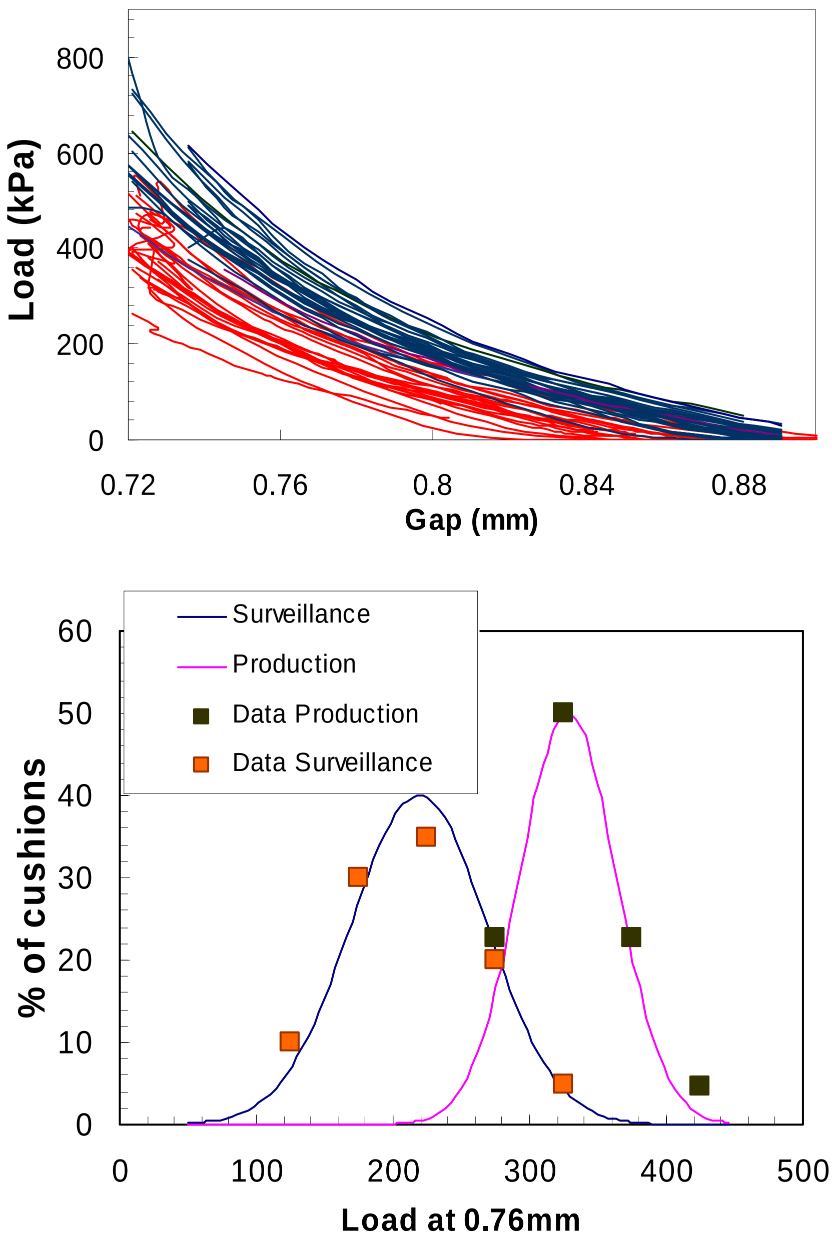


Figure 2. (A) Load vs Deflection curves from Surveillance testing at KCP (courtesy of J. Schnieder). Blue curves: production; Red Curves: surveillance retesting for the same parts. (B) Gaussian distributions of the load at 0.76 mm for cushions at production and at retest. Parts tested represent a range of ages.

2. DATA AND RESULTS

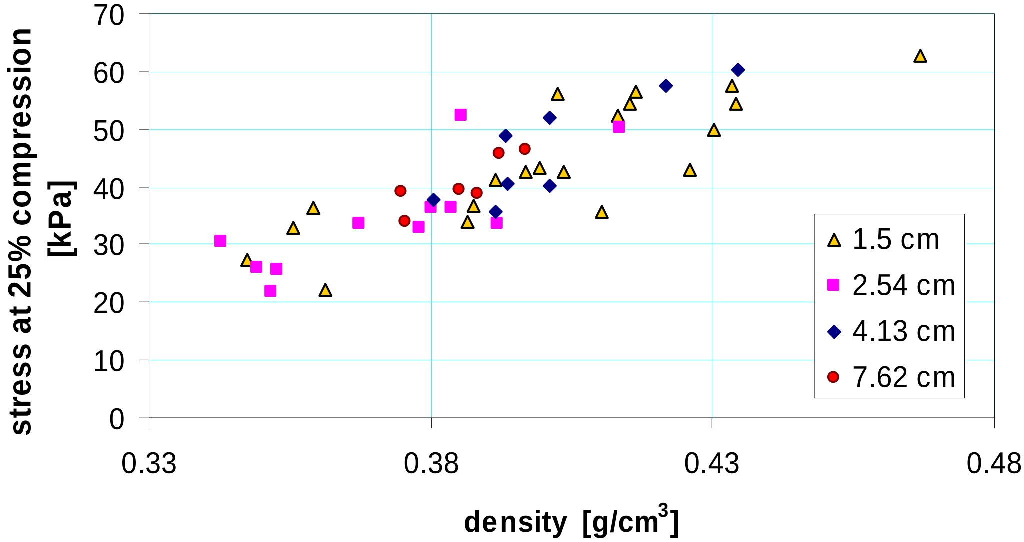
2.1 Review of Surveillance Data

2.1.1 Overview of surveillance data

As of July 2003, there are 18 years of surveillance data from weapon tear downs. Surveillance testing procedures and reporting requirements are documented.[5] Although the entire stress-strain curve for four specified spots are generally acquired in testing, only the average of the four loads required to compress the cushion to 0.76 mm is reported in Cycle reports. (It is our belief that this data is insufficient and that in the future reports containing all the data should be returned to the design agency as part of the surveillance documentation.)

We have obtained full testing reports from KCP on approximately 30 stress cushions and the deflection vs. load behavior is shown in Figure 2A with distributions of the load to reach 0.76 mm for both production and surveillance shown in Figure 2B. These figures document that A) there is a wide distribution of cushion performance for both new and used cushions and B) there is a dramatic drop in load retention in cushions returned from service, presumably due to compression set, but potentially also due to chemical and physical degradation pathways.

The data scatter seen in surveillance testing is likely due to broad distributions of structural and chemical heterogeneity from part to part and within the individual parts as well as distributions in service conditions. A series of tests performed by Los Alamos National Laboratory measured the load at 25% compression as a function of density for a series of low density cushion samples, and the results are shown in Figure 3A.[6] In addition, the distribution of densities across a typical cushion has been measured



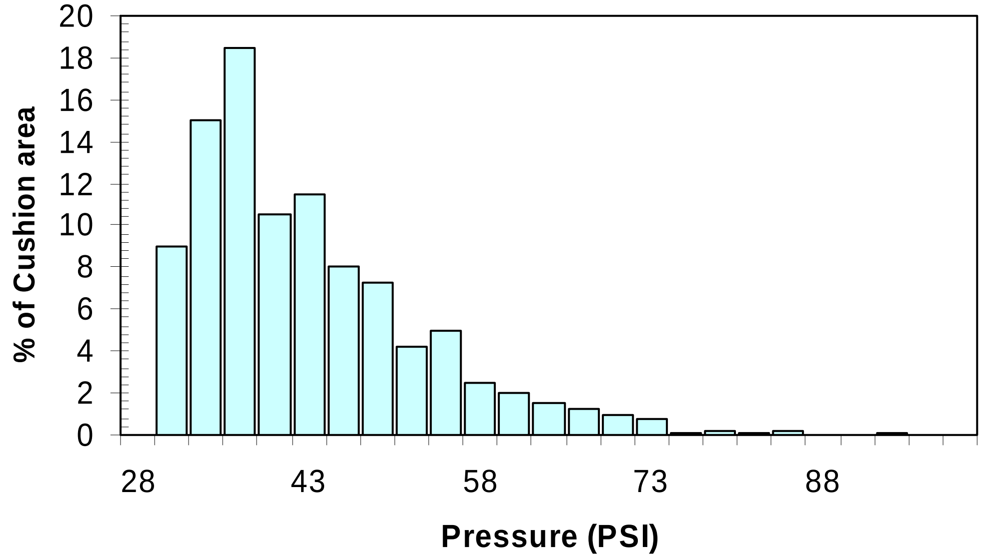


Figure 3. (A) Dependence of load at 25% compression on density for low density S5370 cushions. (B) histogram describing pressure measured by pressure sensitive tape for a compressed pad of low density S5370. Data obtained on coupons cut from one cushion. Stress and densities were measured on each coupon. Since the pressure at a given gap is related to the density, the histogram indirectly provides a measure of the distribution of densities across a cushion. Data courtesy of Tom Stephens (LANL).[6]

indirectly by using pressure sensitive paper to measure the load across a disk shaped low density S5370 pad; these results are shown in Figure 3B.[6] Since no effort is made in production to locate areas of specified density between cushions and there is a distinct distribution of densities across individual cushions, the observed distributions in load retention seen in surveillance are not surprising. Furthermore, it is highly unlikely the cushions are uniformly loaded or that the loading from system to system is similar. LANL PMAP studies (discussed below) have shown a distinct dependence of the aging trends on the degree of compression in service. If a distribution of service compression exists (likely), this would cause further contributions to the broad distributions in cushion surveillance testing results.

2.1.2 Aging trends from Surveillance data

As mentioned above, the testing of the stress cushion involves

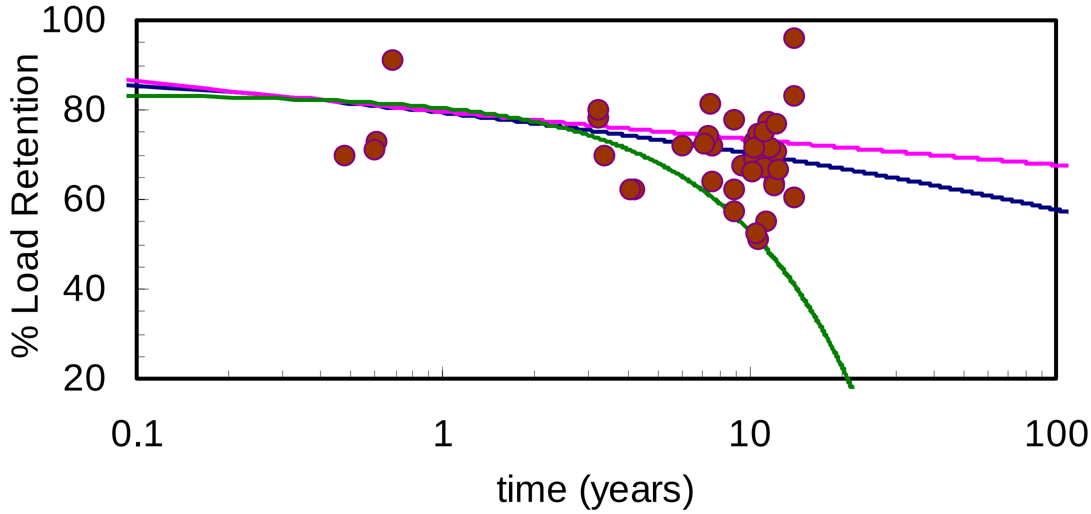


Figure 4. Percent load retention versus time in service for high density S5370 cushions obtained from Surveillance testing. Solid curves are fits to various aging models and predict a wide range of load retention at 60 years total service life.

compression/deflection measurements at four points: one at the pole and three spots 120 degrees apart at locations between the pole and the waist. The average stress at 0.76 mm compressed thickness for the four points is reported both at production and surveillance.

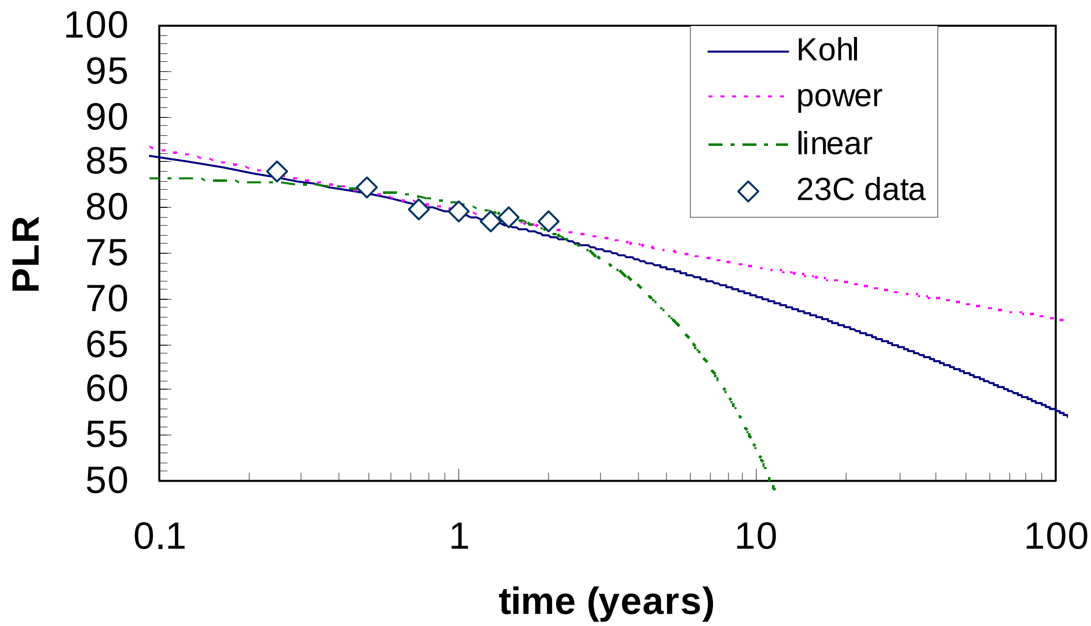


Figure 5. 2-Year KCP data with three representative fits used for lifetime predictions listed in Table 1.

Acceptance requirements at production are that the stress fall between 38.8 and 62.8 PSI. At surveillance retest approximately 80% of stress cushions fall below the 38.8 PSI lower limit for production. Note, however, that this simplistic measurement may be confounded by the fact that the cushions have experienced compression set during their lifetimes and are thus thinner at the time of surveillance.

Generally, in order to assess aging trends, the load measured at surveillance is compared to the load measured at production in an attempt to remove the effects of structural and chemical heterogeneity (the testing positions are marked at production for future retesting):

$$\%\text{load retention (PLR)} = 100*\text{Load}(t)/\text{Load}(0)$$

A plot of PLR as a function of age is shown in Figure 4. This data is characterized by an initial drop in load retention followed by a broad scatter of PLR for ages beyond 3 years. In an initial effort to obtain lifetime predictions for these cushions, three standard aging models have been used to fit the data (models will be discussed in Section 2.2.2 below) and are shown in Figure 4. A broad range of resulting fitting parameters were applicable to the surveillance data and predicted lifetimes from tens to thousands of years. These results graphically illustrate the difficulty in developing accurate aging models for these materials based solely on simplistic surveillance data.

2.2 Review of LANL-PMAP Evaluation

In view of the poor suitability of surveillance data for obtaining lifetime assessments for the S5370 stress cushions, LANL, in collaboration with KCP, designed and executed two tests to measure the time dependence of load retention for cushions stored under compression and at elevated temperatures.[7] These tests have been designated the 2-year and 9-year tests based on the length of time for which data was acquired. To date, the results of these tests are the best basis for lifetime predictions for S5370. A detailed analysis of this data has been attempted by Jim Coons, et al at LANL and form the basis of the development of "age-aware" constitutive equations for these polymers being developed as part of LANL Enhanced Surveillance Campaign (ESC) work.[8]

For the 9-year study, the low density (0.4 g/cc) S5370 samples were subjected to constant compression of 50%, and the only independent variable was storage temperature (23, 50, 60, and 70ºC). Yearly, compression set and compression stress/strain properties were measured after the parts had been allowed to equilibrate for 25 minutes with no compression.

The 2-year study investigated the effects of thickness (0.045, 0.10, and 0.16”), density (0.4 and 0.47 g/cc), temperature (23, 50, and 70ºC), and the degree of compression (20 and 35%) on the load retention of the foam.

These tests, however, were designed to feed lifetime assessments for systems where the dominant form of S5370 was the low density form. LLNL is currently concerned with developing lifetime predictions on the high density version. We review the results of these tests here; however, the results of these tests can be extended to the high density form only with caution.

The percent load retention as a function of time obtained from the 2-year study is shown in Figure 5 and shows a rapid, initial decay in load retention followed by a more steady decrease in load retention at longer times. The initial rapid drop has been attributed to the initial compression set common in these types of materials. The longer term decay in load retention could be due to additional compression set, physical relaxation, or chemical aging mechanisms. It was further observed in these tests that the predominant contribution to the reduction in load retention was from the storage temperature. Aging in higher temperatures environments resulted in lower load retention, as would be expected. Higher compression loadings during aging were observed to result in an increase loss in load retention capability. Finally, the effects of density and thickness were minimal within the range of test parameters investigated.

The stress strain curves obtained for the 9-year study on samples aged at room temperature and 70 ºC are shown in Figure 6, and the load as a function of time,

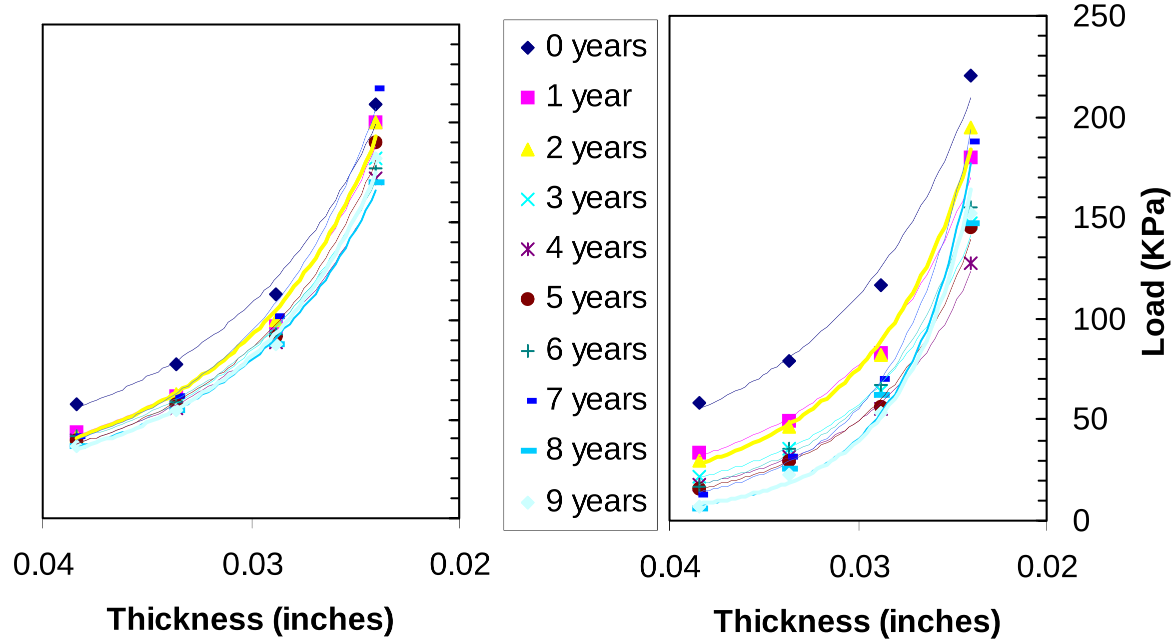


Figure 6. Load versus Deflection curves for low density S5370 cushions obtained from KCP and LANL 9-year aging study. (A) Storage at 20% compression; (B) Storage at 35% compression.

measured at room temperature, is shown in Figure 7 for two degrees of compression (20% and 40%). The data obtained as part of the 9-years study shows similar results to the 2-year study: a rapid loss of load retention of ~10% followed by a slower decrease with increasing time. The 9-year study offers two additional insights: that the long term degradation mechanism is thermally activated and that it depends on the degree of compression.

This bimodal decay of mechanical properties, therefore, can be described in terms of the two regimes of decay: Regime 1) initial reduction in percent load retention (PLR) in first year followed by a less dramatic change over the course of the remaining 2-years, both due to rapid physical aging and stress relaxation (not spin-relaxation, discussed below) and setting; Regime 2) steady decrease in PLR after 3-5 years at a slower rate than found in Regime 1. This behavior is very subtle in the 20% compression 2-year data at 23 °C, but with increased temperature or increasing time (see the 9-year data), the trend is obvious.

For our lifetime estimates below, we have separated the behavior of both aging regimes by fitting the data in two parts. In the case of the 2-year data, the first year has been fit to both a logarithmic and a power law model to simulate the effects of physical aging.[9-13] Data beyond one year has been fit to linear, logarithmic, and exponential decay models appropriate primarily for chemical degradation mechanisms.[9-13] For the 9-year data set, the initial physical aging that presumably occurs within the first 2-years is

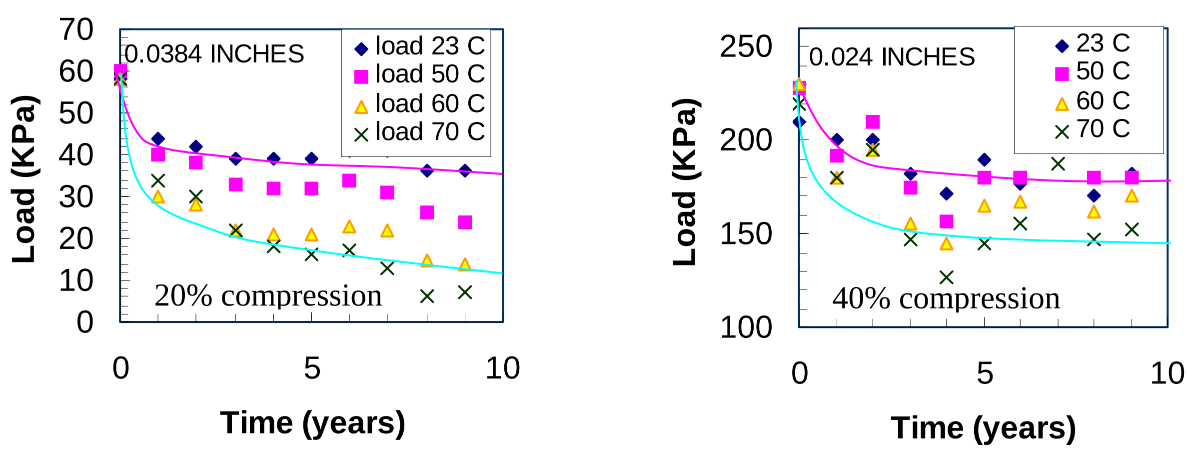


Figure 7. Load at fixed compression versus time from the KCP and LANL 9-year aging study. Load is plotted for compression at 20% and 40% for low density S5370. Power law fits (pink for 23 ºC; blue for 70 ºC) to the data are shown as solid curves and predict 50+/- 10 % load retention at 60 years for long term storage at temperatures below 50 ºC, but lower retention at higher storage temperatures.

ignored and the final data (years 3-9) have been fit to linear, logarithmic, and exponential decay models, again consistent with chemical, or thermal, controlled degradation what ever the mechanism.

2.2.1 Lifetime predictions based on Regime 1

The changes in load retention in the first few years of aging in both the 2-year and 9-year tests can be described by a rapid, initial decrease in load retention (LR) in the first year, followed by a much slower change in LR over the next 4-5 years. This initial “setting” of S5370 can be fit to either a power law or logarithmic function specific for physical relaxation of the composite. Specific results for such fits are listed for the 2-year study (both 20 and 35% compression) in Table 1. Lifetime predictions based on these fits predict a useful lifetime greater than 1000 years as shown in Figure 5 for the 2-year study and Figure 8 for the 9-year data at 20% compression and room temperature service conditions. A fit of the data to an exponential degradation model results in a time to 50% load retention of 18 years.

2.2.2 Lifetime predictions based on Regime 2

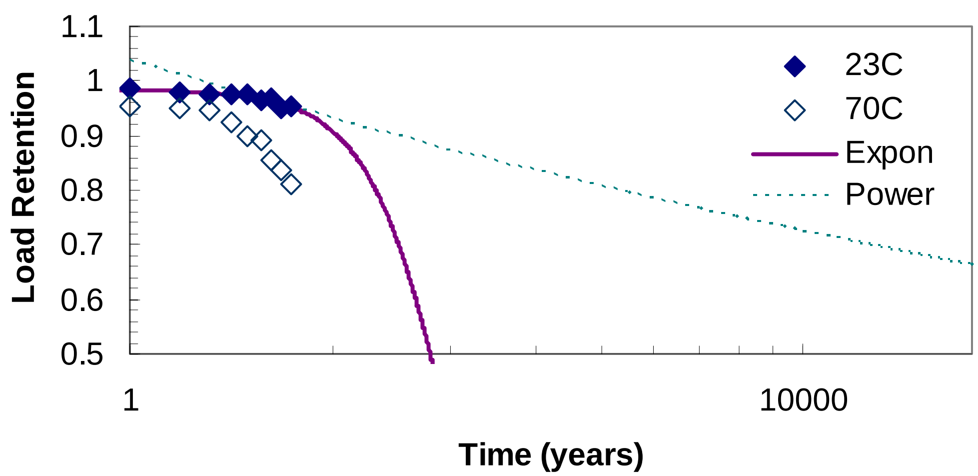


Figure 8. KCP 9-Year data with Fits used to derive lifetime listed in Table 1.

The long-term aging in Regime 2, presumably due to slow physical relaxation or chemical degradation, has been analyzed by fitting the results of the 9-year data after the third year to various models of aging reported in the open literature: 1) linear; 2)

Logarithmic (linear on a semi-log plot); and 3) exponential.[9-13] A fourth model, the Kohlrausch model, has been described in the literature but is too complex for the limited fidelity of the data obtained here.[14-16] There is extensive effort at LANL to develop specific aging models, though these are not developed sufficiently at this time to provide quantitative input for this report.[17]

The exact mathematical forms of the fitting equations can be found in Table 1. The initial physical aging that presumably occurs within the first 2-years, and termed Regime 1 above, is ignored and the final data (years 3-9) have been fit to linear, logarithmic, and exponential decay models. All models provide reasonable fits to the experimental data and the results are tabulated in Table 1 and plotted in Figure 9. It is unknown at this time which, if any, of these models is the correct model to represent the aging phenomena in S5370 foams.

If these fits are used to extrapolate the short-term (0 to 9-years) behavior to longer lifetimes (>20 years), an estimate of the lifetime prediction can be obtained. We have calculated the time to reach 60% (our arbitrary failure criteria) load retention capacity and the PLR at 60 years (our arbitrary minimum lifetime requirement). The results are shown in Table 1. Results range from relatively short lifetimes predicted from linear fits for the 2-year studies to relatively long lifetimes based on logarithmic decay model fits for the 23 °C 20% compression data.

The results of the 2-year and 9-year studies done by KCP seem to suggest that aging of S5370 is likely very slow. Our extrapolations predict that at 60 years the PLR of S5370 should remain above 40% if aging can be described by first order kinetics (exponential decay model with one mechanism). If the PLR follows instead a linear decrease with time, however, a failure is predicted before 60 years.

2.3 Chemical Aging Assessment of S5370

As mentioned previously, the stress cushions are subject to complex chemical and physical stresses. The combination of the two can lead to non-linear changes in material properties with time. Unfortunately, the LANL PMAP studies have, to date, only considered the effects of physical stress under the influence of long term storage at elevated temperature in low density S5370. To gain further insight into chemical and

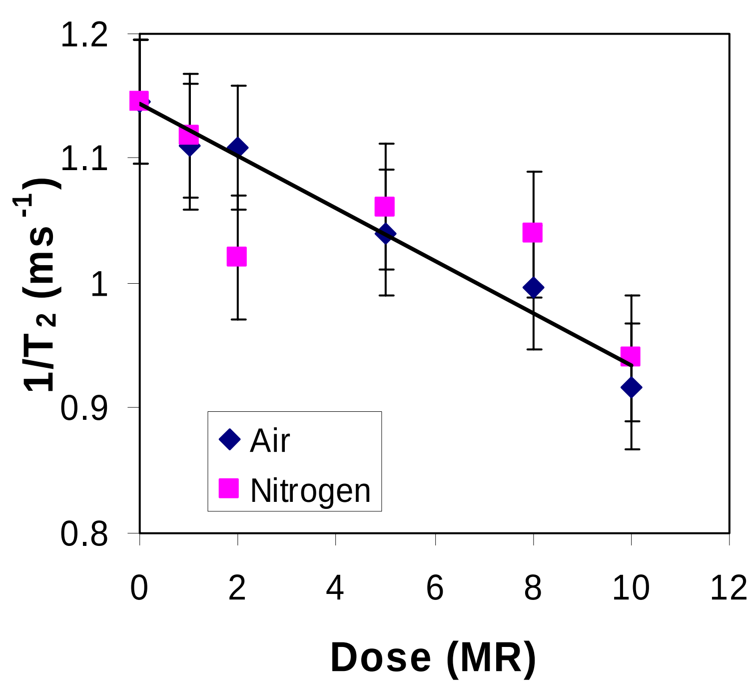


Figure 9. Relative Stiffness by NMR ($1/T_2$ ~ G') for irradiated high density S5370.

physical changes occurring due to alternate degradation pathways, we have initiated a scoping study involving radiation exposure, thermal exposure, desiccation-induced degradation, and so-called multimode degradation studies where parts are subject to simultaneous stressors. The results of these studies are reviewed below, except for the case of desiccative degradation, which will be reviewed separately.

2.3.1 Radiative degradation

The effects of ionizing radiation on the general class of silicone-based polymers is well known to lead to crosslinking and chain scissioning reactions at dose and dose rate dependent rates.[18] The effects on silica filled silicone polymers is less well studied, but in general tends to follow similar trends.[19-23] Previous studies on M97 based siloxanes using solvent swelling, nuclear magnetic resonance (NMR), atomic force microscopy (AFM), and dynamic mechanical analysis (DMA) have documented that the effects of γ-radiation exposure depend on dose, atmosphere, and stress.[19-24] Limited studies have been performed on α-irradiated samples and have shown primarily surface hardening, since the depth penetration of the radiation limits the degradation to a few tens to hundreds of microns.[25] These effects may have important implications for the interfacial interactions between the cushions and the surrounding materials, such as friction and adhesion, but will not significantly change bulk properties such as modulus or segmental mobility.

We have completed similar γ-radiation degradation studies on S5370 in two parts: 1) analysis of RTV-5370 as a conveniently available model material (obtained from the United Kingdom Atomic Weapons Establishment (AWE)); and 2) a small batch of unused S5370 obtained from KCP. The results from the first study have been reported elsewhere and show that at stockpile relevant doses, crosslinking and chain-scissioning reactions have minimal effect on the crosslink density of RTV-5370.[20] (Stockpile relevant doses have been estimated for other systems and have been reported by an LLNL researcher (Mark Mount).[26])

Due to a lack of current production capabilities for high density S5370, solvent swelling and DMA methods were not applied for studying degradation in S5370 by radiation exposure. Since NMR can measure the crosslink density and modulus indirectly through the effect of segmental mobility on these parameters and consumes only ~10 mg of material, NMR was used to study radiation induced changes in crosslink density. The validation of these assumptions for M97 and RTV-5370 based composites has been established and has been assumed here to be valid for S5370 due to the similarity to these materials.[19-23] The results of these studies on S5370 are shown in Figure 9 and indicate

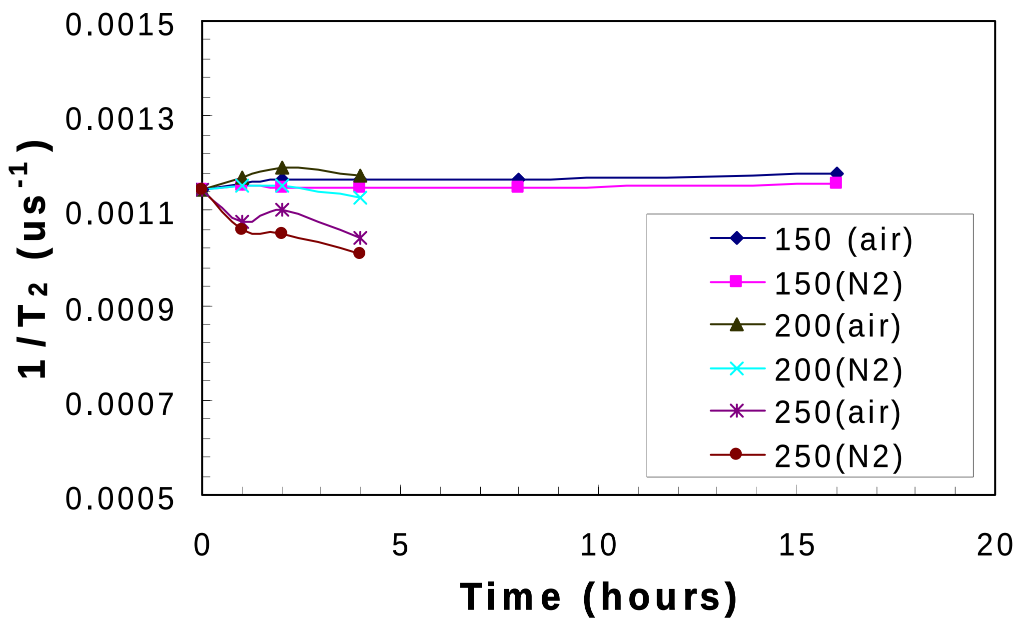


Figure 10. Relative stiffness ($1/T_2$) by NMR for thermally [at the temperatures (in ºC) listed] degraded high density S5370.

that, similar to RTV5370, only minimal changes in crosslink density have been detected in material irradiated to less than 1 MRad cumulative dose, though the degradation in S5370 seems to be dominated at these doses by chain scissioning mechanisms.

2.3.2 Thermal degradation

Previous studies of thermal degradation of filled silicones have shown that these materials can be subject to degradation by chain scissioning and backbiting mechanisms at high temperatures and slow disentanglement of the network structure at low temperatures.[27-32] In order to quantify the effects of thermal degradation, we artificially aged S5370 in N_2 atmospheres for a range of temperatures and times. The results of these studies are shown in Figure 10 and show that only at excessive temperatures does degradation occur to a significant extent. Previous studies by AWE on RTV 5370 silicone have shown similar results.

2.3.4 Thermal degradation in the presence of compression: insights into compression set kinetics

The primary degradation mechanisms active in the LANL and KCP 2 and 9-year studies are thermal degradation and compressive stress degradation leading to a combination of reduction in crosslink density and an increase in compression set with time. Studies on RTV-5370 foams by AWE have shown that there are in fact at least two relevant degradation mechanisms: one active at temperatures less than 100 ºC and one active at temperatures greater than 125 ºC.[31,32] SPME studies of thermal degradation in M97 based silicones have suggested a backbiting mechanism for the high temperature mechanism.[33] Patel and Skinner have postulated that the thermal degradation is in part due to the loss of chain entanglements the lower temperatures which lead to an increase in compression set with time.[31,32] Patel and Skinner also measured the activation energy barrier for the low temperature compression set by time temperature superpositioning techniques to be 22 ± 7 kJ/mol. Jim LeMay[33] fitted long-term accelerated aging compression data obtained by Jim Schnieder at KCP and derived a similar activation energy for sub-100 ºC temperature degradation of M97 of 19.7 kJ/mol and time temperature superposition analysis of the KCP and LANL 2 and 9-year experiments on low density S5370 have measured an activation energy of 25 ± 7 kJ/mol (See Figure 11).

The following power law expression for the time dependent changes in thermally activated compression set for RTV5370 can be derived from the above activation energy:

$$\text{Compression Set\%} = 5.812 * t^{(0.456 + 0.01432*\ln(t))}$$

Using this equation a prediction can be made that the cushion will reach a 25% compression set within 19 yrs. A direct comparison of this prediction with results

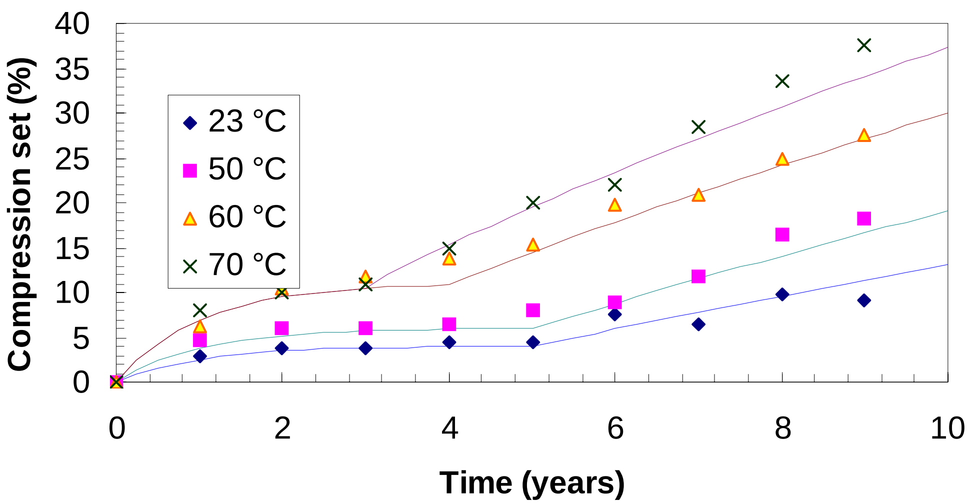


Figure 11. Compression set versus time as measured during KCP and LANL 9-year aging study. Fits to data are dual exponential curves. The change in kinetics with temperature allows the prediction of an activation energy of 25 ± 7 kJ/mol.

obtained during the KCP/LANL 9-year study and data returned from surveillance is shown in Figure 12. A decrease in effect cushion thickness due to compression set would be reflected in a drop in load retention, which is what is generally seen in laboratory and surveillance testing. These tests, however, have not been performed on high density S5370. The high density formulation, in addition, is in service in different loading conditions. As a result, these experiments are currently being performed on high density S5370 under a variety of stockpile relevant conditions to quantify the contribution of thermally activated compression set to the lifetime of these materials.

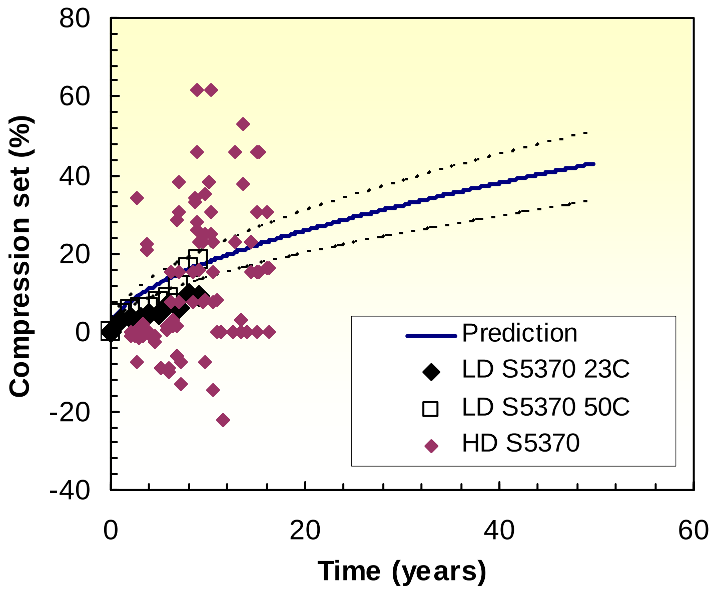


Figure 12. Prediction of compression set based on thermal activated degradation as explained in text compared to experimental data obtained in KCP and LANL 9-year study. High density data obtained from surveillance measurements at KCP.

2.3.5 Radiation plus Compression

Previous studies on M97 cushions have shown that the simultaneous exposure to radiation and compression or tension leads to a dramatic increase in the degree of compression or tensile set.[21] In light of this, two new S5370 specimens were similarly tested: one for control and one for irradiation. Both control and irradiated specimens were subjected to <100 mTorr vacuum for the same duration during each irradiation cycle. Therefore the only difference between the two samples was the gamma dose. Testing was in compression with a precision washer having a thickness corresponding to 15%

compression. Each sample was cycled three times to a point where contact was made

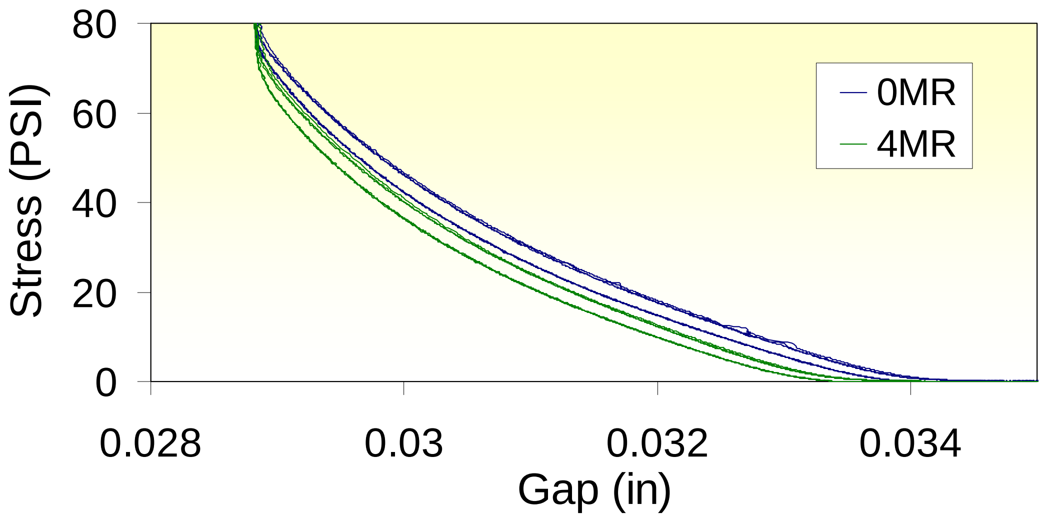


Figure 13. Stress vs. Gap for high density S5370 held under 14% compression and irradiated in vacuum for (Blue) 0 MRad and (Green) 4 MRad. The drop in modulus observed for the 4 MR sample was also seen at 1, 2, and 3 MRad, though to a lesser degree and is due to an increase in the compression set taken during irradiation under compression.

between load platens and washer (observed by a sharp increase in stiffness on curve). Testing was performed after cumulative doses of 0, 0.5, 1.0, 2.0, and 4.0 Mrad. Final testing was without washer to see "lockup" behavior. The results of these studies are shown in Figure 13 and show that, similar to M97, high density S5370 also is subject to an increased degree of compression set when irradiated under compression. Due to this compression set, it would be expected that an additional loss in load would be observed in service.

2.3.7 SR assessments from NMR and stress relaxation measurements.

Due to the complex heterogeneity in S5370, initial efforts at performing standard DMA methods to surveillance return samples of high density S5370 were inconclusive. The DMA data was irreproducible and subject to large variability depending on the position tested and the size of the testing area. In light of this observation, we initiated both NMR and stress relaxation measurements.

It has been noted above that NMR provides information on average crosslink density in these polymers indirectly from ^{1}H relaxation times ($1/T_2$ ~ Crosslink Density (CLD) ~ storage modulus (G')). Figure 14 shows the small increase in crosslink density (and hardening) observed with age for a series of surveillance return parts. The data is in

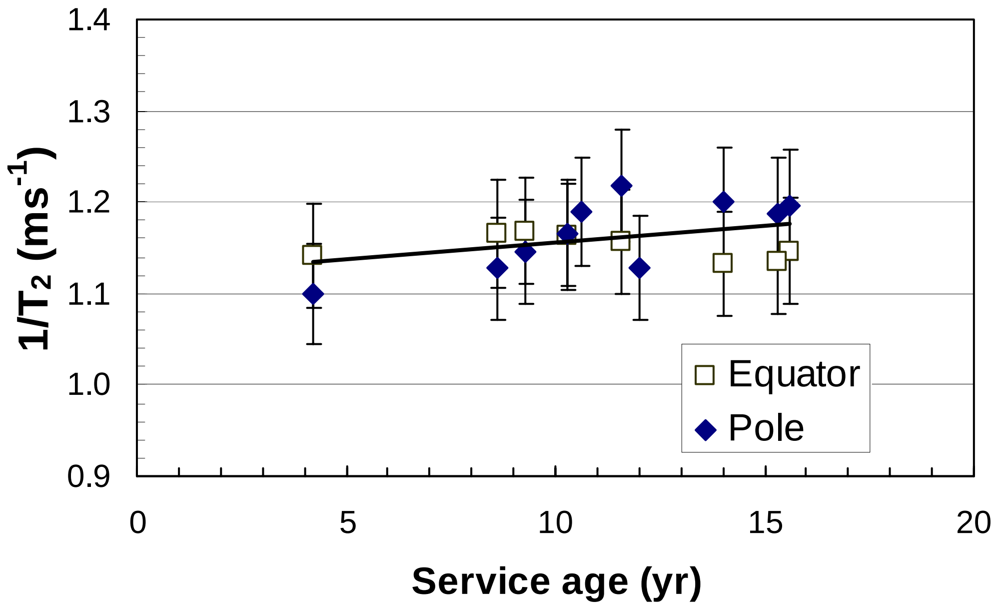


Figure 14. Inverse transverse relaxation time ($1/T_2$) for surveillance return high density S5370 parts. $1/T_2$ has been shown to be a direct probe of segmental dynamics of the polymer chains and thus an indirect probe of crosslink density and elastic modulus. The results suggest that these parts are slowly crosslinking with age.

sharp contrast to the observations based on load retention measured by surveillance of an initial sharp decrease followed by a slow decrease, as shown in Figures 2 and 4. The NMR method is, in general, less sensitive to the effects of pore structure than the surveillance load retention measurements and instead reflects the polymer network structure. The NMR data, therefore, indicate that high density S5370 is subject to slow

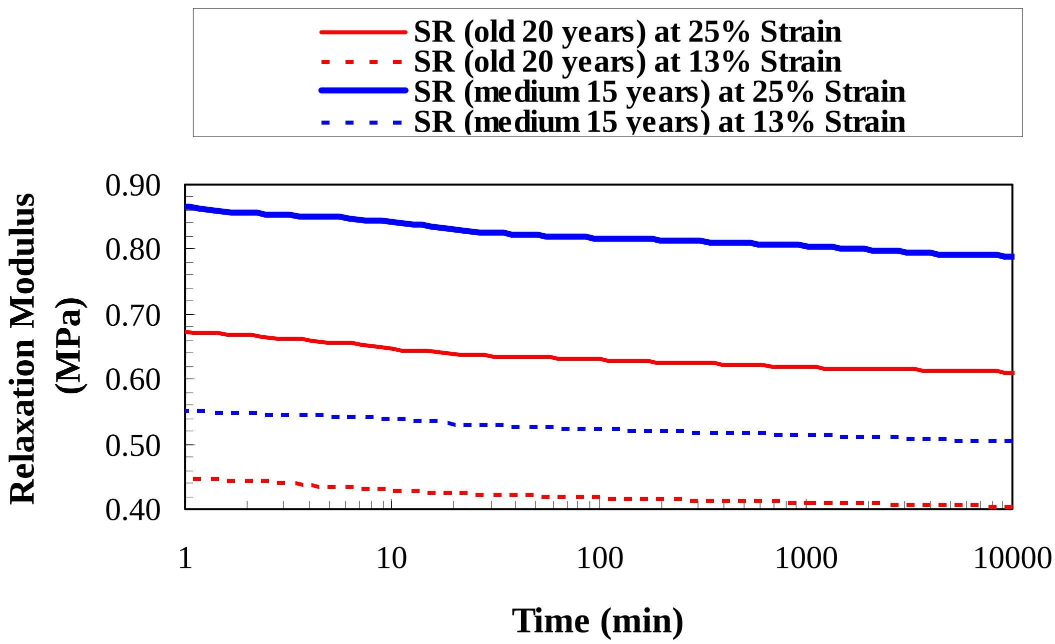


Figure 15. Stress relaxation experiments of high density S5370 cushions returned from surveillance at 13 and 25% Strain. Cushions studies were 15 and 20 years old. Relaxation rates are approximately constant for both cushions while there are differences in initial modulus consistent with NMR results.

crosslinking reactions in service that increase the bulk modulus by 5-10% over 20 years. This increase is stiffness might compensate to a limited extent the loss in load retention seen in these polymers due to compression set.

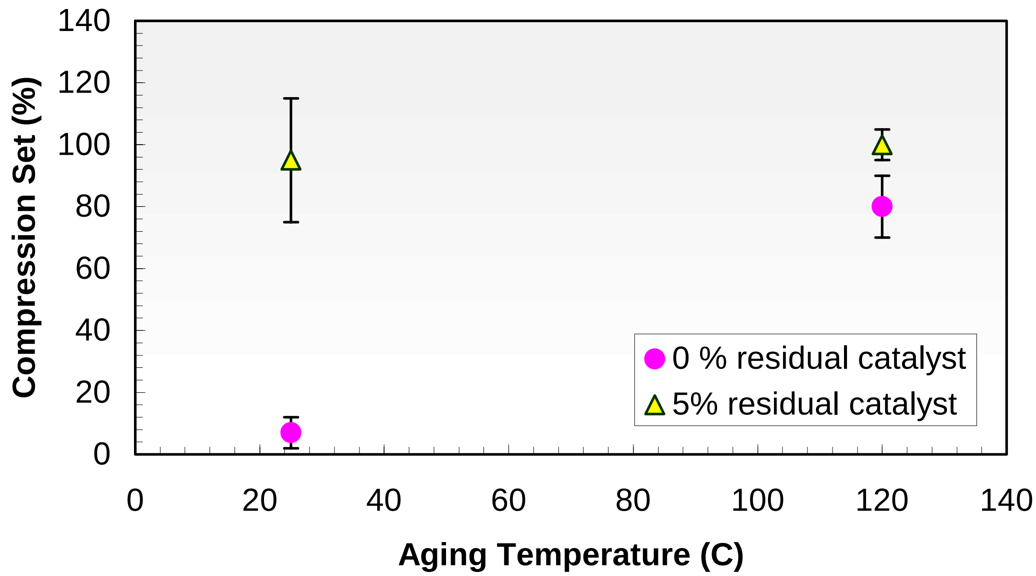


Figure16. Dependence of compression set in low density S5370 cushions on amount of residual tin catalyst added during formation. In general, a significant increase in the compression set was observed with the inclusion of residual catalyst. Increase in compression set at elevated temperatures is expected. Data courtesy of Tom Stephens (LANL).

Stress relaxation experiments were performed on aged high density S5370 cushions and the results are shown in Figure 15. In general for the two samples studied (no pristine material was studied since production capacity of high density S5370 is limited) there is a slow loss of load retention over the course of time. The data can be fit to standard power law relationships and suggests that in service stress relaxation contributes ~10% loss in load over 60 years. No significant difference in relaxation rate with age was observed. Experiments on polysiloxanes with different formulations, however, have shown that additional aging mechanisms cause non-power law behavior at longer times.[27-30] There is no evidence to date that this is of concern in low density S5370, and by analogy to high density S5370. However, work in this area will continue (see conclusions).

2.3.6 Effect of Catalyst variation (From LANL)

A number of reports have documented siloxane polymer performance degradation with varying amounts of residual catalyst (amount of catalyst curing agent added in excess of specifications) due to long term post curing and hydrolysis reactions.[28] LANL and AWE have been examining the effect of residual stannous hexanoate catalyst on the compression set and load retention in low density S5370 and results of some of this work are shown in Figure 16. The experiments performed by LANL have shown that even small amounts of excess catalyst can lead to increased degrees of compression set in these materials over time. Fortunately, AWE studies quantifying catalysts levels in the cushions have shown only small variations from specifications and these amounts are unlikely to lead to part failure. It is possible that some of the variability seen in surveillance testing of the S5370 parts, however, may be due to variability in the catalyst content. To test this hypothesis, AWE has begun preliminary assessments of correlations between variations in catalysts levels and load retention in surveillance return RTV-5370 parts. LLNL will be performing similar assessments on high density S5370 (quantification of tin catalysts and correlation to load retention) in the future.

3.0 Proposed New Aging Tests at LLNL

All specialized mechanical property testing of aged S5370 to date has been done with densities near 0.4 gm/cc. Since the density of the part of interest is much higher, it is proposed that new tests be initiated. These tests are as follows:

1) Long term load retention on high density S5370 material. In this test the part will not be fully relieved of compression during testing, but will be cycled within a small range around the nominal compression value during storage.
2) Assessments of residual catalyst in high density S5370 and correlation to load retention properties
3) Variable temperature compression set measurements in high density S5370 to determine activation energy of thermally activated compression set degradation mechanism(s) in nitrogen atmospheres
4) Development of age-aware lifetime models in collaboration with LANL and AWE efforts on similar formulations

4.0 Conclusions

The results of lifetime predictions based on the KCP and LANL two and nine-year tests of S5370 aging suggest that S5370 is likely long lived. It is probable that the load retention after 60 years will be above 50% of its original value. This lifetime prediction, however, is based on tests with inherent flaws and should be viewed with caution. Based on this fact, further investigations of these materials are warranted. Our specific conclusions, based on the work presented here, are the following:

1) There is an inherently large degree of structural and chemical heterogeneity in S5370 cushions that complicates lifetime assessments;
2) Current surveillance testing procedures are inadequate for providing data for lifetime predictions;

3) LANL PMAP data suggests a 60-year load retention of greater than 40%; however, this is for low density versions and extrapolation to high density must be viewed with caution, and a new set of testing is recommended;
4) Results of chemical aging assessments suggest that radiation damage is minimal at stockpile relevant doses, thermal degradation leads to compression set due to disentaglement of the network structure over time and a negligible amount of chain scissioning at relevant temperatures. The compression set is accelerated by exposure to radiation;
5) In the absence of further testing, a 60-year load retention of greater than 40% of the original value is the best estimate.

5.0 Acknowledgments

The data discussed in this report has been obtained through the cooperation and collaboration of the following people: (LANL) Jim Coons, Matt Lewis, Tom Stephens, (KCP) David Solyom, Rebecca Cohenour, William Sung, Elizabeth Nail, Jim Schneider, (LLNL) Gordon Spellman, Steve DeTeresa, Long Dinh, Bryan Balazs, Jim LeMay.

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Table 1. Results of and extrapolation of results of fits to various aging models to 60% Load Retention.

Data Set	Model	Parameters	Time to 60%LR (yr)	PLR @ 60 yrs
2yr (20%)	linear	A=0.86, B=-0.0245	11.5	0.0
	Log	A=0.83, B=-0.051	10000	0.74
	Power law	A=0.97, B=-0.026	10000	0.8
	Exponential	A=0.86, B=220	50	0.25
2yr (35%)	linear	A=0.83, B=-0.0304	13	0.0
	Log	A=0.80, B=0.0658	1000	0.68
	Power law	A=0.98, B=-0.0352	>3000	
	Exponential	A=0.80, B=50	50	0.25
9yr	Linear-23C[1]	A=1.00, B=-0.0055	80	0.67
	Linear-70C		17	0.0
	Log-23C[2]	A=103.5, B=8.6	102	0.88
	Log-70C			0.50
	Power law[3]	A=1.037, B=-0.0389	>10000	>0.90
	Exp-23C[4]	A= 0.993, B=220	100	0.78
	Exp-70C	A=0.996, B=46.7	14	0.27
	Exp-23C PLR(0)=0.85[5]		85	0.64
Surv. Return Samples	linear	A=0.744, B=-0.00837	17	Unknown
	Log	A=0.78, B=0.13	50	
	Power law	A=0.764, B=-0.0744	21	
	Exponential	n.d.	20	

Mathematical Models used to obtain lifetime predictions shown in the above table:

1. Linear model: PLR=B*time – A
2. Logrithmic model: PLR=A*log(B*time)
3. Power Law model: PLR = A*time^{B}
4. Exponential model: PLR = A*exp(-time/B)
5. Kohlrausch model: PLR = A*exp(-1*(time/B)^{C})

7.0 Appendix: Crystallization phenomena of S5370.

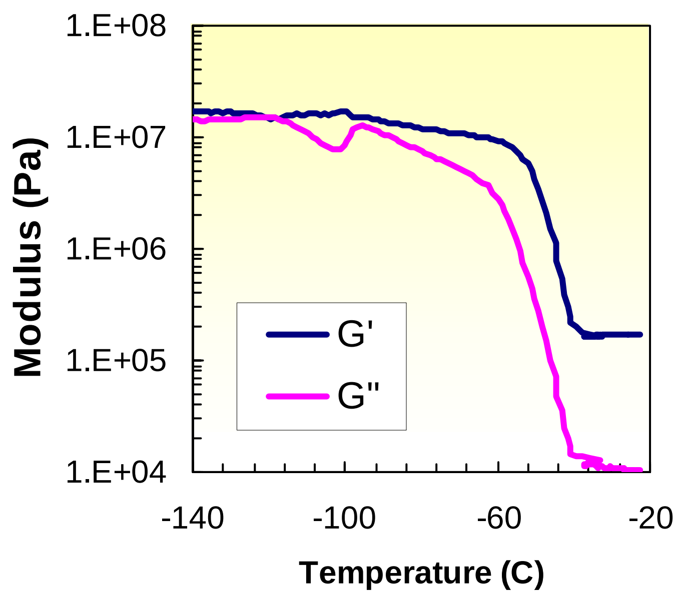

Figure A1. Change in modulus as measured by variable temperature DMA studies on high density S5370. The dramatic increase in modulus near -50 ºC is due to material crystallization documented in DSC studies (not shown).

As part of the baseline efforts associated with the research described in this report, routine DSC and DMA studies indicated that S5370 crystallized at the edges of the system STS. The increase in stiffness as a function of service temperature is shown in Figure A1. These results show that at temperatures near -50 ºC, S5370 hardens significantly as domains crystallize and form additional effective crosslinks. The kinetics of crystallization as a function of temperature are shown in Figure A2 and indicate that at temperatures near the lower end of the STS, crystallization is slow and produces a small increase in hardness. Thermal excursions to temperatures below -55 ºC, however, result in rapid crystallization and hardening.

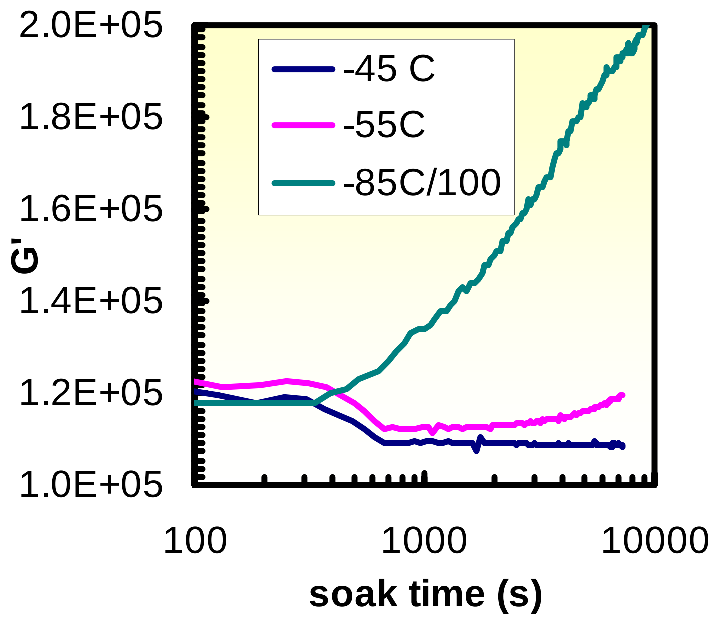

Figure A2. Crystallization kinetics as a function of soak time held at the indicated temperatures for high density S5370.